

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 05-108903 (71)Applicant : NIPPON OIL & FATS CO LTD

(22)Date of filing : 12.04.1993 (72)Inventor : HONDA SUSUMU
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(54) ADMIXTURE FOR CEMENT

(57)Abstract:

PURPOSE: To improve slump loss preventing properties, water reducing properties and workability, comprising an esterified product of a specific copolymer and a polyoxyalkylene derivative.

CONSTITUTION: A polyoxyalkylene derivative of formula I (A1O is 2-4C oxyalkylene and its 50-100mol% is oxyethylene; R is 1-4C alkyl; (n) is 4-150) is copolymerized with maleic anhydride in the molar ratio of 1:0.5-1:2 in the presence of a peroxide-based polymerization initiator or an azo-based polymerization initiator, optionally with another radically polymerizable component to give (A) a copolymer, which is reacted with (B) a polyoxyalkylene derivative of formula II (R²-3 are 1-4C alkyl; A2O is 2-4C oxyalkylene; (m) is 1-300) in the ratio of the number of equivalents of acid anhydride group of maleic anhydride unit of the component A and the number of equivalents of hydroxyl group of the component B of 1:2-10:1 in the presence of an alkali, an amine, etc., as a catalyst or dehydrated in the presence of an aid catalyst or heated in the absence of the catalyst and esterified.



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CLAIMS

[Claim(s)]

[Claim 1] (A) Component (b) general formula [1]

CH₂=CHCH₂O(A₁O) nR₁ -- [1]

the polyoxyalkylene derivative shown by (however, the 50 - 100-mol % is [the alkyl group of carbon numbers 1-4 and n of an oxyethylene radical and R₁] 4-150 in the oxy-alkylene group of carbon numbers 2-4 for A₁O), and (**) -- the copolymerization object which uses a maleic anhydride as an indispensable component, and (B) component general formula [2]

R₂, R₃, and N(A₂O) mH -- [2]

It is the additive for cement which consists of an esterification reactant with the polyoxyalkylene derivative shown by (however, R₂ and R₃ are [the oxy-alkylene group of carbon numbers 2-4 and m of the alkyl group of carbon numbers 1-4 and A₂O] 1-300).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the additive for cement.

[0002]

[Description of the Prior Art] Conventionally, the naphthalenesulfonic acid formaldehyde condensate salt, the melamine sulfonic-acid formaldehyde condensate salt, the ligninsulfonic acid salt, etc. are used as a water reducing agent as an additive of cement compounds, such as concrete. The demand of high intensity increases to concrete and the need of lessening the amount of the water in a concrete constituent appeared in it in recent years. Although it was effective in the above-mentioned additive lessening the amount of the water in a concrete constituent, the fluid fall of the concrete constituent which happens with time, i.e., slump loss, was unavoidable. Various proposals are made in order to prevent this slump loss. Although the compound with water reducing agents, such as fine-particles-like an olefin and a maleic-anhydride copolymerization object, and a naphthalenesulfonic acid formalin condensate, is proposed by JP,60-16851,A, separation tends to occur in it and there is a trouble which becomes uneven in it. Although it is indicated by JP,59-162162,A that concomitant use with a naphthalenesulfonic acid formalin condensate salt or a melamine sulfonic-acid formalin condensate salt, and an allyl alcohol alkylene oxide addition product-partial saturation dicarboxylic acid copolymerization object is effective in prevention of slump loss, it is not necessarily enough. Although the copolymer of the polyoxyalkylene partial saturation ether and a maleic anhydride, its hydrolyzate, or the salt of that hydrolyzate is proposed by JP,63-285140,A, the field of prevention of slump loss in this case is not necessarily enough for it. Although the copolymerization object of the polyoxyalkylene partial saturation ether and a maleate is proposed by JP,2-163108,A, there is a trouble that the setting time is long in it.

[0003]

[Problem(s) to be Solved by the Invention] Prevention of the above-mentioned slump loss is the big concerns of the concrete industry, and it was anxious for quick solution. The purpose of this invention is excellent in the slump loss prevention effectiveness, and its water reducing nature is large, and is to offer the good additive for cement of workability on the occasion of use.

[0004]

[Means for Solving the Problem] In order that this invention persons may get the additive for cement which has the above-mentioned desirable property, wholeheartedly, as a result of research, they find out that the reactant of a specific copolymerization component and the nitride which has a specific oxy-alkylene group suits the purpose of this invention, and came to complete this invention based on this knowledge. That is, this invention is (A) component (b) general formula [1].

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[0005] This invention is explained below at a detail. The additive for this invention cement consists of a reactant of the copolymer of the above-mentioned (A) component, and the nitride which has the oxy-alkylene group of the (B) component. As an oxy-alkylene group of the carbon numbers 2-4 shown by A₁O of the general formula [1] used for the (A) component of this invention, an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are raised, and the 50 - 100-mol % is an oxyethylene radical. When an oxyethylene radical is less than [50 mol %], since water solubility is inadequate, high water reducing nature cannot be obtained. As an alkyl group of the carbon numbers 1-4 shown by R₁ of a general formula [1], a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and a tertiary butyl radical are raised. In the case of less than four, n of a general formula [1] will be 4-150, coagulation becomes slow, if larger than 150, viscosity will become high and manufacture will become difficult. As an alkyl group of the carbon numbers 1-4 shown by R₂ and R₃ of a general formula [2], a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and a tertiary butyl radical are raised. As an oxy-alkylene group of the carbon numbers 2-4 shown by A₂O of a general formula [2], an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are raised. The copolymerization object of the compound of a general formula [1] and a maleic anhydride can be easily obtained by carrying out copolymerization of the compound and maleic anhydride of a general formula [1] using a peroxide system polymerization initiator or an azo system polymerization initiator.

Copolymerization of the component in which other copolymerization of styrene, an alpha olefin, vinyl acetate, etc. is possible may be mixed and carried out in that case. Although the ratio of the compound of a general formula [1] and a maleic anhydride is 1:0.5-1:2 in a mole ratio, it is 1:0.9 to 1:1.2 more preferably. As for the ratio of the copolymerization object of the compound of a general formula [1], and a maleic anhydride, and the compound of a general formula [2], 1:2-10:1 are desirable at the ratio of the acid-anhydride radical number of equivalent of the maleic-anhydride unit of a copolymerization object, and the number of equivalent of the hydroxyl group of the compound of a general formula [2].

[0006] The reactant of the copolymer of the compound of a general formula [1] and maleic anhydride which are the (A) component of this invention, and the compound of the general formula [2] which is the (B) component is an esterification object, and can be easily manufactured by making alkali or amines, such as a potassium hydroxide, a sodium hydroxide, and sodium methylate, etc. react as a catalyst. Moreover, also by dehydrating using the acid catalyst of Para toluenesulfonic acid etc., it can manufacture and can manufacture also by heating with a non-catalyst further. this invention cement additive can be obtained instead of the above-mentioned manufacture approach also by one sort of a maleic anhydride and a maleic acid, or two sorts of copolymerization reactions according to the maleate and ** need for the compound of ** general formula [1], and the compound of ** general formula [2]. When a maleic anhydride is added, a copolymerization reaction and an ester exchange reaction occur, and the same this invention additive as said manufacture approach can be manufactured.

[0007] The amount of the additive used of this invention is 0.04 - 1 % of the weight preferably 0.02 to 2% of the weight to cement. The additive of this invention may be used together with other additives, such as a naphthalenesulfonic acid formalin condensate salt, a melamine sulfonic-acid formaldehyde condensate salt, and a polycarboxylic acid system compound, or a defoaming agent, an air entraining agent, a rusr-proofer, a setting accelerator, retarding admixture, etc. As a polycarboxylic acid system compound, there are a salt of the copolymerization object of the compound of a general formula [1] and a maleic anhydride, the copolymerization object of the methacrylic ester of the polyoxyethylene monomethyl ether and methacrylate, and the copolymerization object of styrene and a maleic anhydride, a salt of the copolymerization object of an olefin and a maleic anhydride, polyacrylate, a polymethacrylic acid salt, etc. As an additive of this invention, alkali, such as a potassium hydroxide, a

sodium hydroxide, and a calcium hydroxide, and amines may be mixed.

[0008]

[Example]

The copolymerization object of the compound of a general formula [1] and a maleic anhydride is shown in the example 1 of manufacture - the 10 1st table. It taught the 4 opening flask to which churning equipment, nitrogen entrainment tubing, a thermometer, and reflux tubing were attached by the ratio of weight % which showed the compound of a general formula [2] shown with the copolymerization object in the 2nd table in the 2nd table. Furthermore, 0.1% of the weight of the sodium methylate of a copolymerization object was added, and 100 degrees C was made to react for 3 hours. The weight average molecular weight of the obtained reactant is shown in the 2nd table.

[0009]

[Table 1]

第1表

共重合物名	一般式 [1] の化合物	(モル)	無水マレイイン酸 (モル)	他の单量体 (モル)	重量平均分子量
A	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₁₁ CH ₃	(1. 0)	1. 0	—	18, 000
B	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₃₃ CH ₃	(1. 0)	1. 0	—	20, 000
C	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₁₁ CH ₃	(1. 0)	1. 0	—	30, 000
D	CH ₂ =CHCH ₂ O{[(C ₃ H ₆ O) ₁₅ (C ₂ H ₄ O) ₁₅ }C ₄ H ₉] ¹⁰ }(C ₂ H ₄ O) ₁₁ CH ₃	(1. 0)	1. 0	—	24, 000
E	CH ₂ =CHCH ₂ O{[(C ₂ H ₄ O) ₄₀ (C ₄ H ₈ O) ₁₆ }C ₄ H ₉] ¹⁰ }(C ₂ H ₄ O) ₁₁ CH ₃	(1. 0)	1. 0	—	22, 000
F	CH ₂ =CHCH ₂ O(C ₃ H ₆ O) ₅ (C ₂ H ₄ O) ₃₀ CH ₃	(1. 0)	1. 0	—	23, 000
G	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₁₁ CH ₃	(0. 9)	1. 0	スチレン(0. 1)	18, 000

[0010] Notes 1{ } It is shown that inside is a random-like adduct.
 2) C4H8O shows an oxy-tetramethylen radical.

[0011]

[Table 2]

第2表

製造例	共重合物名 (重量%)	一般式 [2] の化合物 (重量%)	重量平均 分子量
1 A	(55.3)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(44.7) 26,000
2 B	(75.4)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(24.6) 27,000
3 B	(87.7)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(12.3) 23,000
4 B	(52.0)	(CH ₃) ₂ N(C ₂ H ₄ O) ₃₃ H	(48.0) 28,000
5 B	(39.9)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁₀ H	(60.1) 30,000
6 C	(90.4)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(9.6) 30,000
7 D	(52.0)	(C ₂ H ₅) ₂ N[(C ₃ H ₆ O) ₁₅ (C ₂ H ₄ O) ₁₅]H ¹⁾	(48.0) 29,000
8 E	(49.4)	(C ₄ H ₉) ₂ N[(C ₂ H ₄ O) ₄₀ (C ₄ H ₈ O) ₁₀]H ¹¹²⁾	(50.6) 28,000
9 F	(51.8)	(CH ₃) ₂ N(C ₃ H ₆ O) ₅ (C ₂ H ₄ O) ₃₀ H	(48.2) 29,000
10 G	(53.5)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(46.5) 27,000

[0012] Notes 1{ } It is shown that inside is a random-like adduct.
 2) C4H8O shows an oxy-butylene radical.

It mixed by the ratio of weight % which showed other additives shown with the esterification object shown in the example 11 of manufacture - the 14 2nd table in the 3rd table all over the 3rd table, and

mixture was obtained.

[0013]

[Table 3]

第3表

製造例	第2表で示した反応物 (重量%)	他の添加物 (重量%)
1 1	製造例 2 (30.0)	ナフタリンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
1 2	製造例 2 (30.0)	メラミンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
1 3	製造例 2 (50.0)	第1表に示す共重合物A (50.0)
1 4	製造例 3 (50.0)	第1表に示す共重合物B (50.0)

[0014] The trial by concrete was carried out using the reactant and mixture corresponding to the examples 1-14 of manufacture as one to example 14 example. A combination presentation and a test condition are shown below.

Combination presentation (kg/m³)

Water 166 cement 450 sand 681 crushed stones 1032 additives It is shown in the 4th table.

Water / cement ratio 36.9% fine total aggregate ratio It took out, after kneading each component of the 39.9% above for 2 minutes for a pan mixer, and the slump and the air content were measured.

Furthermore, it moved to the collapse type mixer, and mixed by per minute 2 rotation, and the slump and air content of 30 minutes, 60 minutes, and 90 minutes after were measured. Moreover, it measured also about the setting time and compressive strength, and these results were shown in the 4th table.

The same trial as examples 1-14 was performed by making into the example of a comparison the compound shown in the 1-6th examples of a comparison. The result is shown in the 4th table.

Example 1 of a comparison Example 2 of a naphthalenesulfonic acid formalin condensate sodium salt comparison Example 3 of a polyethylene-glycol monoallyl ether-maleic-acid copolymerization object sodium salt comparison Compound 75wt% of the example 1 of a comparison The example [of a comparison / 2 / compound 25wt% of] example 4 of a mixture comparison copolymerization of the 1st table -- a name -- example 5 of a copolymerization object comparison of the compound of a general formula [1] and maleic anhydride which were used by A copolymerization of the 1st table -- a name -- the compound of the general formula [1] used by A, and the monoester ghost by the polyoxyethylene monomethyl ether of a maleic acid -- example of copolymerization object comparison 6 Since the example 6 of a -additive-less comparison cannot knead cement mixture unless it makes [many] water The combination presentation was changed as follows.

Combination presentation (kg/m³)

Water 195 cement 450 sand 652 crushed stones 985 water / cement ratio 43.3% fine total aggregate ratio 40.0% [0015]

[Table 4]

第4表-1

		添加量 (対セメントwt%)	スランプ(cm)				空気量(%)			
			混練直後	30分後	60分後	90分後	混練直後	30分後	60分後	90分後
実 施 例	1	0.30	18.0	19.5	20.5	19.0	4.0	4.1	4.2	4.2
	2	0.28	18.0	19.0	20.0	19.0	4.1	4.1	4.2	4.1
	3	0.24	18.5	19.0	19.0	18.0	4.1	4.0	4.0	3.9
	4	0.32	17.5	18.5	20.0	19.5	4.0	4.1	4.2	4.3
	5	0.38	17.5	19.0	19.5	19.0	3.9	4.2	4.1	4.3
	6	0.30	18.0	19.0	19.5	18.5	4.0	4.0	4.0	3.8
	7	0.33	18.0	18.5	18.5	18.0	4.1	4.2	4.4	4.3
	8	0.40	18.5	19.0	18.5	17.5	4.1	4.2	4.2	4.2
	9	0.38	18.0	18.5	19.0	18.5	3.9	4.1	4.2	4.1
	10	0.30	17.5	19.0	20.0	18.5	4.0	4.1	4.1	4.2
	11	0.50	18.0	17.5	17.5	17.0	4.0	3.9	3.8	3.8
	12	0.60	18.5	17.5	17.0	16.5	4.1	4.0	4.0	3.9
	13	0.20	18.0	18.5	18.0	17.5	4.0	3.0	3.9	3.9
	14	0.22	18.0	19.0	18.5	18.0	4.0	4.1	4.0	3.9
比 較 例	1	0.75	18.0	16.0	13.5	11.5	4.0	3.8	3.7	3.6
	2	0.60	17.5	16.0	14.5	12.5	4.0	4.0	3.9	4.0
	3	0.70	18.0	16.0	13.5	12.5	4.0	4.0	3.9	3.8
	4	0.30	18.5	17.5	16.5	15.5	4.1	4.0	4.0	3.8
	5	0.50	18.5	19.0	18.5	18.0	3.9	4.0	4.1	4.1
	6	-	17.5	16.5	15.5	14.0	4.1	3.9	3.9	3.8

[0016]
[Table 5]

第4表-2

		凝結時間(時間一分)		圧縮強度(kgf/cm ²)		
		始発	終結	3日	7日	28日
実 施 例	1	6-30	8-10	460	625	778
	2	6-00	7-45	467	633	798
	3	5-50	7-30	471	643	801
	4	6-05	7-55	459	634	786
	5	6-00	7-50	468	635	788
	6	5-30	7-15	472	642	799
	7	7-00	8-40	456	622	766
	8	6-50	8-40	458	631	769
	9	7-10	8-55	449	618	761
	10	6-30	8-15	466	630	782
	11	6-15	8-00	449	628	774
	12	6-30	8-20	448	615	768
	13	5-30	7-10	469	632	786
	14	5-50	7-35	467	640	791
比 較 例	1	5-50	7-40	437	611	752
	2	9-00	10-55	429	613	755
	3	7-50	9-40	430	620	757
	4	8-20	10-00	442	630	762
	5	9-50	11-45	451	631	778
	6	5-15	7-00	312	467	605

[0017] example of comparison 1- to a slump index becoming small with time and a fluidity of 6 [4 and] decreasing, a slump index does not become small with time, but, as for examples 1-14, the fluidity is held. As for the examples 2 and 5 of a comparison, the setting time is long. Moreover, since a fixed slump index cannot be obtained unless it makes [many] the amount of water, but the amount of water can be lessened if the additive of this invention is used compared with small compressive strength and a fixed slump index can be obtained when you have no additive, compressive strength is large.

[0018]

[Effect of the Invention] By making the reactant of the copolymer of the polyoxyalkylene derivative of copolymerization nature, and a maleic anhydride, and a specific polyoxyalkylene derivative with a nitrogen atom into an active principle, the additive of this invention is an object which has high slump loss tightness and high water reducing nature, and has the outstanding workability.

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The additive for cement which consists of an esterification reactant with the polyoxyalkylene derivative shown by (however, R₂ and R₃ are [the oxy-alkylene group of carbon numbers 2-4 and m of the alkyl group of carbon numbers 1-4 and A₂O] 1-300) is offered.

[0005] This invention is explained below at a detail. The additive for this invention cement consists of a reactant of the copolymer of the above-mentioned (A) component, and the nitride which has the oxy-alkylene group of the (B) component. As an oxy-alkylene group of the carbon numbers 2-4 shown by A₁O of the general formula [1] used for the (A) component of this invention, an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are raised, and the 50 - 100-mol % is an oxyethylene radical. When an oxyethylene radical is less than [50 mol %], since water solubility is inadequate, high water reducing nature cannot be obtained. As an alkyl group of the carbon numbers 1-4 shown by R₁ of a general formula [1], a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and a tertiary butyl radical are raised. In the case of less than four, n of a general formula [1] will be 4-150, coagulation becomes slow, if larger than 150, viscosity will become high and manufacture will become difficult. As an alkyl group of the carbon numbers 1-4 shown by R₂ and R₃ of a general formula [2], a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and a tertiary butyl radical are raised. As an oxy-alkylene group of the carbon numbers 2-4 shown by A₂O of a general formula [2], an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are raised. The copolymerization object of the compound of a general formula [1] and a maleic anhydride can be easily obtained by carrying out copolymerization of the compound and maleic anhydride of a general formula [1] using a peroxide system polymerization initiator or an azo system polymerization initiator.

Copolymerization of the component in which other copolymerization of styrene, an alpha olefin, vinyl acetate, etc. is possible may be mixed and carried out in that case. Although the ratio of the compound of a general formula [1] and a maleic anhydride is 1:0.5-1:2 in a mole ratio, it is 1:0.9 to 1:1.2 more preferably. As for the ratio of the copolymerization object of the compound of a general formula [1], and a maleic anhydride, and the compound of a general formula [2], 1:2-10:1 are desirable at the ratio of the acid-anhydride radical number of equivalent of the maleic-anhydride unit of a copolymerization object, and the number of equivalent of the hydroxyl group of the compound of a general formula [2].

[0006] The reactant of the copolymer of the compound of a general formula [1] and maleic anhydride which are the (A) component of this invention, and the compound of the general formula [2] which is the (B) component is an esterification object, and can be easily manufactured by making alkali or amines, such as a potassium hydroxide, a sodium hydroxide, and sodium methylate, etc. react as a catalyst. Moreover, also by dehydrating using the acid catalyst of Para toluenesulfonic acid etc., it can manufacture and can manufacture also by heating with a non-catalyst further. this invention cement additive can be obtained instead of the above-mentioned manufacture approach also by one sort of a maleic anhydride and a maleic acid, or two sorts of copolymerization reactions according to the maleate and ** need for the compound of ** general formula [1], and the compound of ** general formula [2]. When a maleic anhydride is added, a copolymerization reaction and an ester exchange reaction occur, and the same this invention additive as said manufacture approach can be manufactured.

[0007] The amount of the additive used of this invention is 0.04 - 1 % of the weight preferably 0.02 to 2% of the weight to cement. The additive of this invention may be used together with other additives, such as a naphthalenesulfonic acid formalin condensate salt, a melamine sulfonic-acid formaldehyde condensate salt, and a polycarboxylic acid system compound, or a defoaming agent, an air entraining agent, a rusr-proofer, a setting accelerator, retarding admixture, etc. As a polycarboxylic acid system compound, there are a salt of the copolymerization object of the compound of a general formula [1] and a maleic anhydride, the copolymerization object of the methacrylic ester of the polyoxyethylene monomethyl ether and methacrylate, and the copolymerization object of styrene and a maleic anhydride, a salt of the copolymerization object of an olefin and a maleic anhydride, polyacrylate, a polymethacrylic acid salt, etc. As an additive of this invention, alkali, such as a potassium hydroxide, a

sodium hydroxide, and a calcium hydroxide, and amines may be mixed.

[0008]

[Example]

The copolymerization object of the compound of a general formula [1] and a maleic anhydride is shown in the example 1 of manufacture - the 10 1st table. It taught the 4 opening flask to which churning equipment, nitrogen entrainment tubing, a thermometer, and reflux tubing were attached by the ratio of weight % which showed the compound of a general formula [2] shown with the copolymerization object in the 2nd table in the 2nd table. Furthermore, 0.1% of the weight of the sodium methylate of a copolymerization object was added, and 100 degrees C was made to react for 3 hours. The weight average molecular weight of the obtained reactant is shown in the 2nd table.

[0009]

[Table 1]

第1表

共重合物名	一般式 [1] の化合物	(モル)	無水マレイン酸 (モル)	他の单量体 (モル)	重量平均分子量
A	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₁₁ CH ₃	(1. 0)	1. 0	—	18,000
B	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₃₃ CH ₃	(1. 0)	1. 0	—	20,000
C	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₁₁₆ CH ₃	(1. 0)	1. 0	—	30,000
D	CH ₂ =CHCH ₂ O{[(C ₃ H ₆ O) ₁₅ (C ₂ H ₄ O) ₁₅]C ₄ H ₉ D}	(1. 0)	1. 0	—	24,000
E	CH ₂ =CHCH ₂ O{[(C ₂ H ₄ O) ₄₀ (C ₄ H ₈ O) ₁₀]C ₄ H ₉ D2}	(1. 0)	1. 0	—	22,000
F	CH ₂ =CHCH ₂ O(C ₃ H ₆ O) ₅ (C ₂ H ₄ O) ₃₀ CH ₃	(1. 0)	1. 0	—	23,000
G	CH ₂ =CHCH ₂ O(C ₂ H ₄ O) ₁₁ CH ₃	(0. 9)	1. 0	スチレン(0. 1)	18,000

[0010] Notes 1{ } It is shown that inside is a random-like adduct.
 2) C4H8O shows an oxy-tetramethylen radical.

[0011]

[Table 2]

第2表

製造例	共重合物名 (重量%)	一般式 [2] の化合物	(重量%)	重量平均分子量
1 A	(55.3)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(44.7)	26,000
2 B	(75.4)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(24.6)	27,000
3 B	(87.7)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(12.3)	23,000
4 B	(52.0)	(CH ₃) ₂ N(C ₂ H ₄ O) ₃₃ H	(48.0)	28,000
5 B	(39.9)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁₀ H	(60.1)	30,000
6 C	(90.4)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(9.6)	30,000
7 D	(52.0)	(C ₂ H ₅) ₂ N[(C ₃ H ₆ O) ₁₅ (C ₂ H ₄ O) ₁₅]H ¹⁾	(48.0)	29,000
8 E	(49.4)	(C ₄ H ₉) ₂ N[(C ₂ H ₄ O) ₄₀ (C ₄ H ₈ O) ₁₀]H ^{1,2)}	(50.6)	28,000
9 F	(51.8)	(CH ₃) ₂ N(C ₃ H ₆ O) ₅ (C ₂ H ₄ O) ₃₀ H	(48.2)	29,000
10 G	(53.5)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(46.5)	27,000

[0012] Notes 1{ } It is shown that inside is a random-like adduct.
 2) C4H8O shows an oxy-butylene radical.

It mixed by the ratio of weight % which showed other additives shown with the esterification object shown in the example 11 of manufacture - the 14 2nd table in the 3rd table all over the 3rd table, and

mixture was obtained.

[0013]

[Table 3]

第3表

製造例	第2表で示した反応物 (重量%)	他の添加物 (重量%)
1 1	製造例2 (30.0)	ナフタリンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
1 2	製造例2 (30.0)	メラミンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
1 3	製造例2 (50.0)	第1表に示す共重合物A (50.0)
1 4	製造例3 (50.0)	第1表に示す共重合物B (50.0)

[0014] The trial by concrete was carried out using the reactant and mixture corresponding to the examples 1-14 of manufacture as one to example 14 example. A combination presentation and a test condition are shown below.

Combination presentation (kg/m³)

Water 166 cement 450 sand 681 crushed stones 1032 additives It is shown in the 4th table.

Water / cement ratio 36.9% fine total aggregate ratio It took out, after kneading each component of the 39.9% above for 2 minutes for a pan mixer, and the slump and the air content were measured.

Furthermore, it moved to the collapse type mixer, and mixed by per minute 2 rotation, and the slump and air content of 30 minutes, 60 minutes, and 90 minutes after were measured. Moreover, it measured also about the setting time and compressive strength, and these results were shown in the 4th table.

The same trial as examples 1-14 was performed by making into the example of a comparison the compound shown in the 1-6th examples of a comparison. The result is shown in the 4th table.

Example 1 of a comparison Example 2 of a naphthalenesulfonic acid formalin condensate sodium salt comparison Example 3 of a polyethylene-glycol monoallyl ether-maleic-acid copolymerization object sodium salt comparison Compound 75wt% of the example 1 of a comparison The example [of a comparison / 2 / compound 25wt% of] example 4 of a mixture comparison copolymerization of the 1st table -- a name -- example 5 of a copolymerization object comparison of the compound of a general formula [1] and maleic anhydride which were used by A copolymerization of the 1st table -- a name -- the compound of the general formula [1] used by A, and the monoester ghost by the polyoxyethylene monomethyl ether of a maleic acid -- example of copolymerization object comparison 6 Since the example 6 of a -additive-less comparison cannot knead cement mixture unless it makes [many] water The combination presentation was changed as follows.

Combination presentation (kg/m³)

Water 195 cement 450 sand 652 crushed stones 985 water / cement ratio 43.3% fine total aggregate ratio 40.0% [0015]

[Table 4]

第4表-1

	添加量 (対セメントwt%)	スランプ(cm)				空気量(%)				
		混練直後	30分後	60分後	90分後	混練直後	30分後	60分後	90分後	
実 施 例	1	0.30	18.0	19.5	20.5	19.0	4.0	4.1	4.2	4.2
	2	0.28	18.0	19.0	20.0	19.0	4.1	4.1	4.2	4.1
	3	0.24	18.5	19.0	19.0	18.0	4.1	4.0	4.0	3.9
	4	0.32	17.5	18.5	20.0	19.5	4.0	4.1	4.2	4.3
	5	0.38	17.5	19.0	19.5	19.0	3.9	4.2	4.1	4.3
	6	0.30	18.0	19.0	19.5	18.5	4.0	4.0	4.0	3.8
	7	0.33	18.0	18.5	18.5	18.0	4.1	4.2	4.4	4.3
	8	0.40	18.5	19.0	18.5	17.5	4.1	4.2	4.2	4.2
	9	0.38	18.0	18.5	19.0	18.5	3.9	4.1	4.2	4.1
	10	0.30	17.5	19.0	20.0	18.5	4.0	4.1	4.1	4.2
	11	0.50	18.0	17.5	17.5	17.0	4.0	3.9	3.8	3.8
	12	0.60	18.5	17.5	17.0	16.5	4.1	4.0	4.0	3.9
	13	0.20	18.0	18.5	18.0	17.5	4.0	3.0	3.9	3.9
	14	0.22	18.0	19.0	18.5	18.0	4.0	4.1	4.0	3.9
比 較 例	1	0.75	18.0	16.0	13.5	11.5	4.0	3.8	3.7	3.6
	2	0.60	17.5	16.0	14.5	12.5	4.0	4.0	3.9	4.0
	3	0.70	18.0	16.0	13.5	12.5	4.0	4.0	3.9	3.8
	4	0.30	18.5	17.5	16.5	15.5	4.1	4.0	4.0	3.8
	5	0.50	18.5	19.0	18.5	18.0	3.9	4.0	4.1	4.1
	6	-	17.5	16.5	15.5	14.0	4.1	3.9	3.9	3.8

[0016]
[Table 5]

第4表-2

		凝結時間(時間一分)		圧縮強度(kgf/cm ²)		
		始発	終結	3日	7日	28日
実 施 例	1	6-30	8-10	460	625	778
	2	6-00	7-45	467	633	798
	3	5-50	7-30	471	643	801
	4	6-05	7-55	459	634	786
	5	6-00	7-50	468	635	788
	6	5-30	7-15	472	642	799
	7	7-00	8-40	456	622	766
	8	6-50	8-40	458	631	769
	9	7-10	8-55	449	618	761
	10	6-30	8-15	466	630	782
	11	6-15	8-00	449	628	774
	12	6-30	8-20	448	615	768
	13	5-30	7-10	469	632	786
	14	5-50	7-35	467	640	791
比 較 例	1	5-50	7-40	437	611	752
	2	9-00	10-55	429	613	755
	3	7-50	9-40	430	620	757
	4	8-20	10-00	442	630	762
	5	9-50	11-45	451	631	778
	6	5-15	7-00	312	467	605

[0017] example of comparison 1- to a slump index becoming small with time and a fluidity of 6 [4 and] decreasing, a slump index does not become small with time, but, as for examples 1-14, the fluidity is held. As for the examples 2 and 5 of a comparison, the setting time is long. Moreover, since a fixed slump index cannot be obtained unless it makes [many] the amount of water, but the amount of water can be lessened if the additive of this invention is used compared with small compressive strength and a fixed slump index can be obtained when you have no additive, compressive strength is large.

[0018]

[Effect of the Invention] By making the reactant of the copolymer of the polyoxyalkylene derivative of copolymerization nature, and a maleic anhydride, and a specific polyoxyalkylene derivative with a nitrogen atom into an active principle, the additive of this invention is an object which has high slump loss tightness and high water reducing nature, and has the outstanding workability.

[Translation done.]

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(54)【発明の名称】セメント用添加剤

(57)【要約】

【構成】 (A) 成分 (イ) 一般式 $CH_2=CHCH_2O$ (A^1O)_n R¹ で示されるポリオキシアルキレン誘導体と (ロ) 無水マレイン酸とを必須成分とする共重合物と (B) 成分一般式 $R^2\cdot R^3\cdot N(A^2O)_nH$ で示されるポリオキシアルキレン誘導体とのエステル化反応物からなるセメント用添加剤。

【目的】 本発明の目的は、スランプロス防止効果が優れ、減水性が大きく、かつ使用に際し作業性の良いセメント用の添加剤を提供することにある。

【特許請求の範囲】

【請求項1】 (A) 成分 (イ) 一般式 [1]



(ただし、 A^1O は炭素数2～4のオキシアルキレン基でその50～100モル%はオキシエチレン基、 R^1 は炭素数1～4のアルキル基、 n は4～150である)で示されるポリオキシアルキレン誘導体と(ロ)無水マレイン酸とを必須成分とする共重合物と(B) 成分一般式 [2]



(ただし、 R^2 と R^3 は炭素数1～4のアルキル基、 A^2O は炭素数2～4のオキシアルキレン基、 m は1～300である)で示されるポリオキシアルキレン誘導体とのエステル化反応物からなるセメント用添加剤。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明はセメント用添加剤に関する。

【0002】

【従来の技術】 従来より、コンクリート等、セメント配合物の添加剤として、ナフタリンスルホン酸ホルムアルデヒド縮合物塩、メラミンスルホン酸ホルムアルデヒド縮合物塩、リグニンスルホン酸塩等が減水剤として用いられている。近年コンクリートには、高強度の要求が高まり、コンクリート組成物中の水の量を少なくする必要性が出てきた。上記添加剤はコンクリート組成物中の水の量を少なくする効果はあるが、経時に起こるコンクリート組成物の流動性の低下、すなわち、スランプロスを避けることはできなかった。このスランプロスを防止するために、種々の提案がなされている。特開昭60-16851号公報には、粉体状のオレフィン・無水マレイン酸共重合物とナフタリンスルホン酸ホルマリン縮合物等の減水剤との配合物が提案されているが、分離が起きやすく、不均一となる問題点がある。特開昭59-162162号公報には、ナフタリンスルホン酸ホルマリン縮合物塩またはメラミンスルホン酸ホルマリン縮合物塩とアリルアルコールアルキレンオキシド付加物-不飽和ジカルボン酸共重合物との併用がスランプロスの防止に有効であることが開示されているが、必ずしも十分ではない。特開昭63-285140号公報には、ポリオキシアルキレン不飽和エーテルと無水マレイン酸との共重合体、その加水分解物またはその加水分解物の塩が提案されているが、この場合もスランプロスの防止の面で必ずしも十分でない。特開平2-163108号公報には、ポリオキシアルキレン不飽和エーテルとマレイン酸エステルとの共重合物が提案されているが、凝結時間が長いという問題点がある。

【0003】

【発明が解決しようとする課題】 上記スランプロスの防止は、コンクリート業界の大きな関心事であり、早期の

解決が切望されていた。本発明の目的は、スランプロス防止効果が優れ、減水性が大きく、かつ使用に際し作業性の良いセメント用の添加剤を提供することにある。

【0004】

【課題を解決するための手段】 本発明者らは、上記の好ましい性質を有するセメント用添加剤を得るために研究の結果、特定の共重合成分と特定のオキシアルキレン基を有する窒素化合物との反応物が本発明の目的に適合することを見いだし、この知見に基づき本発明を完成するに至った。すなわち、本発明は(A) 成分 (イ) 一般式 [1]



(ただし、 A^1O は炭素数2～4のオキシアルキレン基でその50～100モル%はオキシエチレン基、 R^1 は炭素数1～4のアルキル基、 n は4～150である)で示されるポリオキシアルキレン誘導体と(ロ)無水マレイン酸とを必須成分とする共重合物と(B) 成分一般式 [2]



(ただし、 R^2 と R^3 は炭素数1～4のアルキル基、 A^2O は炭素数2～4のオキシアルキレン基、 m は1～300である)で示されるポリオキシアルキレン誘導体とのエステル化反応物からなるセメント用添加剤を提供するものである。

【0005】 以下に本発明を詳細に説明する。本発明セメント用添加剤は、上記(A) 成分の共重合体と(B) 成分のオキシアルキレン基を有する窒素化合物との反応物からなるものである。本発明の(A) 成分に用いる一般式 [1] の A^1O で示される炭素数2～4のオキシアルキレン基としては、オキシエチレン基、オキシプロピレン基、オキシブチレン基およびオキシテトラメチレン基があげられ、その50～100モル%はオキシエチレン基である。オキシエチレン基が50モル%未満の場合は、水溶性が不十分のため高い減水性を得ることができない。一般式 [1] の R^1 で示される炭素数1～4のアルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、ブチル基、イソブチル基および第三ブチル基があげられる。一般式 [1] の n は4～150であり、4未満の場合は凝結が遅くなり、150より大きいと粘度が高くなり製造が困難となる。一般式 [2] の R^2 と R^3 で示される炭素数1～4のアルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、ブチル基、イソブチル基および第三ブチル基があげられる。一般式 [2] の A^2O で示される炭素数2～4のオキシアルキレン基としては、オキシエチレン基、オキシプロピレン基、オキシブチレン基およびオキシテトラメチレン基があげられる。一般式 [1] の化合物と無水マレイン酸との共重合物は、一般式 [1] の化合物と無水マレイン酸とを過酸化物系重合開始剤あるいはアゾ系重合開始剤を用いて共重合させることにより容易に得

ことができる。その際、ステレン、 α -オレフィン、酢酸ビニル等の他の共重合可能な成分を混合して共重合させてもよい。一般式【1】の化合物と無水マレイン酸との比率はモル比で1:0.5~1:2であるが、より好ましくは1:0.9~1:1.2である。一般式【1】の化合物と無水マレイン酸との共重合物と一般式【2】の化合物との比率は共重合物の無水マレイン酸単位の酸無水物基当量数と一般式【2】の化合物の水酸基の当量数の比で1:2~10:1が好ましい。

【0006】本発明の(A)成分である一般式【1】の化合物と無水マレイン酸との共重合体と(B)成分である一般式【2】の化合物との反応物はエステル化物であり、水酸化カリウム、水酸化ナトリウム、ナトリウムメチラート等のアルカリ類あるいはアミン類等を触媒として反応させることにより、容易に製造することができる。また、パラトルエンスルホン酸等の酸触媒を用いて脱水することによっても製造でき、さらに無触媒で加熱することによっても製造することができる。本発明セメント添加剤は、上記製造方法の代わりに、①一般式【1】の化合物と②一般式【2】の化合物のマレイン酸エステルと③必要により無水マレイン酸、マレイン酸の1種または2種との共重合反応によっても得ることができる。無水マレイン酸を添加した場合には、共重合反応及びエステル交換反応が起こり、前記製造方法と同一の本発明添加剤を製造することができる。

【0007】本発明の添加剤の使用量はセメントに対して0.02~2重量%、好ましくは0.04~1重量%で

ある。本発明の添加剤は、ナフタリンスルホン酸ホルマリン縮合物塩、メラミンスルホン酸ホルムアルデヒド縮合物塩、ポリカルボン酸系化合物等の他の添加剤、あるいは消泡剤、空気連行剤、防錆剤、凝結促進剤、凝結延長剤等と併用しても良い。ポリカルボン酸系化合物としては、一般式【1】の化合物と無水マレイン酸との共重合物、ポリオキシエチレンモノメチルエーテルのメタクリル酸エステルとメタクリル酸塩との共重合物、ステレンと無水マレイン酸との共重合物の塩、オレフィンと無水マレイン酸との共重合物の塩、ポリアクリル酸塩、ポリメタクリル酸塩等がある。本発明の添加剤として、水酸化カリウム、水酸化ナトリウム、水酸化カルシウム等のアルカリ類、およびアミン類を混合しても良い。

【0008】

【実施例】

製造例1~10

第1表に一般式【1】の化合物と無水マレイン酸との共重合物を示す。その共重合物と第2表に示した一般式【2】の化合物とを、第2表に示した重量%の比率で、攪拌装置、空素吹き込み管、温度計、還流管の付いた四つロフラスコに仕込んだ。さらに、共重合物の0.1重量%のナトリウムメチラートを加え100°C、3時間反応させた。得られた反応物の重量平均分子量を第2表に示す。

【0009】

【表1】

第1表

共重合物名	一般式 [1] の化合物	(モル)	無水マレイン酸 (モル)	他の单量体 (モル)	重量平均分子量
A	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{11}\text{CH}_3$	(1.0)	1.0	—	18,000
B	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{13}\text{CH}_3$	(1.0)	1.0	—	20,000
C	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{11}\text{CH}_3$	(1.0)	1.0	—	30,000
D	$\text{CH}_2=\text{CHCH}_2\text{O}\{(\text{C}_3\text{H}_6\text{O})_{15}(\text{C}_2\text{H}_4\text{O})_{15}\}\text{C}_4\text{H}_9$	(1.0)	1.0	—	24,000
E	$\text{CH}_2=\text{CHCH}_2\text{O}\{(\text{C}_2\text{H}_4\text{O})_{40}(\text{C}_2\text{H}_4\text{O})_{10}\}\text{C}_4\text{H}_9$	(1.0)	1.0	—	22,000
F	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_5(\text{C}_2\text{H}_4\text{O})_{30}\text{CH}_3$	(1.0)	1.0	—	23,000
G	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{11}\text{CH}_3$	(0.9)	1.0	スチレン(0.1)	18,000

【0010】注1) () 内はランダム状付加体であることを示す。

2) $\text{C}_4\text{H}_8\text{O}$ はオキシテトラメチレン基を示す。

【0011】
【表2】

第2表

製造例	共重合物名 (重量%)	一般式 [2] の化合物	(重量%)	重量平均 分子量
1 A	(55.3)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(44.7)	26,000
2 B	(75.4)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(24.6)	27,000
3 B	(87.7)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(12.3)	23,000
4 B	(52.0)	(CH ₃) ₂ N(C ₂ H ₄ O) ₅ H	(48.0)	28,000
5 B	(39.9)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(60.1)	30,000
6 C	(90.4)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(9.6)	30,000
7 D	(52.0)	(C ₂ H ₅) ₂ N[(C ₃ H ₆ O) ₁₅ (C ₂ H ₄ O) ₁₅]H	(48.0)	29,000
8 E	(49.4)	(C ₄ H ₉) ₂ N[(C ₂ H ₄ O) ₄₀ (C ₄ H ₈ O) ₁₆]H	(50.6)	28,000
9 F	(51.8)	(CH ₃) ₂ N(C ₃ H ₆ O) ₅ (C ₂ H ₄ O) ₅₀ H	(48.2)	29,000
10 G	(53.5)	(CH ₃) ₂ N(C ₂ H ₄ O) ₁₁ H	(46.5)	27,000

【0012】注1) () 内はランダム状付加体である 40 剤とを第3表中に示した重量%の比率で混合し、混合物ことを示す。

2) C₄H₈Oはオキシブチレン基を示す。

製造例11～14

第2表で示したエステル化物と第3表に示した他の添加

を得た。

【0013】

【表3】

第3表

製造例	第2表で示した反応物 (質量%)	他の添加物 (質量%)
11	製造例2 (30.0)	ナフタリンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
12	製造例2 (30.0)	メラミンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
13	製造例2 (50.0)	第1表に示す共重合物A (50.0)
14	製造例3 (50.0)	第1表に示す共重合物B (50.0)

【0014】実施例1～14

実施例として製造例1～14に対応する反応物および混合物を用いてコンクリートによる試験を実施した。配合組成、試験条件を次に示す。

配合組成 (kg/m³)

水 166

セメント 450

砂 681

碎石 1032

添加剤 第4表に示す。

水/セメント比 36.9%

細骨材率 39.9%

上記の各成分を強制練りミキサーにとり、2分間練り混ぜたのち取り出し、スランプおよび空気量を測定した。さらに可倒式ミキサーに移し、毎分2回転で混合し、30分後、60分後、90分後のスランプおよび空気量を測定した。また凝結時間、圧縮強度についても測定を行い、これらの結果を第4表に示した。

比較例1～6

次に示す化合物を比較例として、実施例1～14と同様の試験を行った。その結果を第4表に示す。

比較例1 ナフタリンスルホン酸ホルマリン縮合物ナト

リウム塩

比較例2 ポリエチレングリコールモノアリルエーテル-マレイン酸共重合物ナトリウム塩

比較例3 比較例1の化合物75wt%、比較例2の化合物25wt%の混合物

比較例4 第1表の共重合物名Aで使用した一般式
[1]の化合物と無水マレイン酸との共重合物

比較例5 第1表の共重合物名Aで使用した一般式
[1]の化合物とマレイン酸のポリオキシエチレンモノ

メチルエーテルによるモノエステル化物との共重合物

比較例6 添加剤なし

比較例6は水を多くしないとセメント混合物を混練することができないので配合組成を次のように変更した。

配合組成 (kg/m³)

水 195

セメント 450

砂 652

碎石 985

水/セメント比 43.3%

細骨材率 40.0%

【0015】

【表4】

第4表-1

	添加量 (対セメントwt%)	スランプ(cm)				空気量(%)			
		混練直後	30分後	60分後	90分後	混練直後	30分後	60分後	90分後
実 施 例	1 0.30	18.0	19.5	20.5	19.0	4.0	4.1	4.2	4.2
	2 0.28	18.0	19.0	20.0	19.0	4.1	4.1	4.2	4.1
	3 0.24	18.5	19.0	19.0	18.0	4.1	4.0	4.0	3.9
	4 0.32	17.5	18.5	20.0	19.5	4.0	4.1	4.2	4.3
	5 0.38	17.5	19.0	19.5	19.0	3.9	4.2	4.1	4.3
	6 0.30	18.0	19.0	19.5	18.5	4.0	4.0	4.0	3.8
	7 0.33	18.0	18.5	18.5	18.0	4.1	4.2	4.4	4.3
	8 0.40	18.5	19.0	18.5	17.5	4.1	4.2	4.2	4.2
	9 0.38	18.0	18.5	19.0	18.5	3.9	4.1	4.2	4.1
	10 0.30	17.5	19.0	20.0	18.5	4.0	4.1	4.1	4.2
	11 0.50	18.0	17.5	17.5	17.0	4.0	3.9	3.8	3.8
	12 0.60	18.5	17.5	17.0	16.5	4.1	4.0	4.0	3.9
	13 0.20	18.0	18.5	18.0	17.5	4.0	3.0	3.9	3.9
	14 0.22	18.0	19.0	18.5	18.0	4.0	4.1	4.0	3.9
比 較 例	1 0.75	18.0	16.0	13.5	11.5	4.0	3.8	3.7	3.6
	2 0.60	17.5	16.0	14.5	12.5	4.0	4.0	3.9	4.0
	3 0.70	18.0	16.0	13.5	12.5	4.0	4.0	3.9	3.8
	4 0.30	18.5	17.5	16.5	15.5	4.1	4.0	4.0	3.8
	5 0.50	18.5	19.0	18.5	18.0	3.9	4.0	4.1	4.1
	6 -	17.5	16.5	15.5	14.0	4.1	3.9	3.9	3.8

【0016】

【表5】

第4表-2

		凝結時間(時間一分)		圧縮強度(kgf/cm ²)		
		始発	終結	3日	7日	28日
実 施 例	1	6-30	8-10	460	625	778
	2	6-00	7-45	467	633	798
	3	5-50	7-30	471	643	801
	4	6-05	7-55	459	634	786
	5	6-00	7-50	468	635	788
	6	5-30	7-15	472	642	799
	7	7-00	8-40	456	622	766
	8	6-50	8-40	458	631	769
	9	7-10	8-55	449	618	761
	10	6-30	8-15	466	630	782
	11	6-15	8-00	449	628	774
	12	6-30	8-20	448	615	768
	13	5-30	7-10	469	632	786
	14	5-50	7-35	467	640	791
比較 例	1	5-50	7-40	437	611	752
	2	9-00	10-55	429	613	755
	3	7-50	9-40	430	620	757
	4	8-20	10-00	442	630	762
	5	9-50	11-45	451	631	778
	6	5-15	7-00	312	467	605

【0017】比較例1～4、6は経時的にスランプ値が小さくなり、流動性が少なくなるのに対し、実施例1～14は経時的にスランプ値が小さくならず、流動性が保持されている。比較例2および5は凝結時間が長くなっている。また添加剤なしの場合は、水の量を多くしないと一定のスランプ値を得ることができず、圧縮強度が小さいのに比べ、本発明の添加剤を使用すると水の量を少なくして一定のスランプ値を得ることができるため、圧

縮強度が大きくなっている。

【0018】

【発明の効果】本発明の添加剤は共重合性のポリオキシアルキレン誘導体と無水マレイン酸との共重合体と空素原子を持つ特定のポリオキシアルキレン誘導体との反応物を有効成分とすることにより、高いスランプ防止性、高い減水性を有し、かつ優れた作業性を有する物である。